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Development of Abrasion Resistant Glass-Ceramics From Industrial Waste Products

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TABLE OF CONTENTS

		Page Number
	SUMMARY	ii
1.	INTRODUCTION	1
2.	OBJECTIVE	2
3.	EXPERIMENTAL	2
	3.1 Composition of the Glasses	2
	3.2 Preparation of Glasses	2
	3.3 Dilatometric Measurements	5
	3.4 Nucleation and Crystallization of the glasses	5
	3.5 X-Ray Diffractometry	5
	3.6 Abrasion Testing Apparatus	6
	3.7 Four-Point Bending Tests	6
	3.8 SEM Examination	7
4.	RESULTS AND DISCUSSION	
	4.1 Dilatometry	7
	4.2 Controlled Devitrification and Phase Identification	8
	4.3 Abrasion Resistance	12
	4.4 Modulus of Rupture	21
	4.5 Optical Microscopy	24
	4.6 SEM Analysis	24
5.	CONCLUSIONS AND RECOMMENDATIONS	43
6.	ACKNOWLEDGEMENT	43
	APPENDIX A: Literature Survey on Slag-Ceramics	44

SUMMARY

Slagceramics were produced from glass compositions using pelletized slag, obtained from the National Slag Association in Hamilton, as the major ingredient. The abrasion resistance, fracture toughness and microstructure of the prepared glass and glass-ceramics were evaluated. Glasceramics with good abrasion resistance were obtained when iron oxide in conjunction with carbon was used as a nucleating agent.

1. INTRODUCTION

Slagceramics which are produced from blast-furnace slag or other compositionally similar slags by a process of glass making and controlled devitrification, belong tothe general class of materials known as glass-ceramics.

Glass-ceramics are known to have a higher mechanical strength and a greater abrasion resistance than the parent glasses. Among the various kinds of glass-ceramics, the slagceramics have been found to have excellent abrasion resistance. Slag, being a waste product, is reasonably cheap and, therefore, the slagceramics can be economically produced by the building materials industry for the construction of floor tiles, spouts, pipelines, and bases subject to abrasion.

The Department of Energy, Mines and Resources over the past three years has sponsored a program for the development of abrasion resistant materials at the Ontario Research Foundation. The preceding Final Report No. 67042-81 (Development of Abrasion Resistant Glass-Ceramics, DSS File No: 18SQ.23440-9-9081-1, Contract Serial No. OSQ80-00197) focussed on an investigation of abrasion resistant ceramics by varying the composition and nucleation time. The results were encouraging enough to initiate the present phase of the program, development of abrasion resistant glass-ceramics by varying the nucleating agents and soak times.

This report describes the development of slagceramics using the slag which is a waste product of the steel making process of Dofasco. The glass-ceramics have been evaluated for their abrasion resistance and mechanical strength.

2. OBJECTIVE

The objective of the EMR Slag Ceramics program was to develop and study new glass-ceramic compositions from industrial slags which show abrasion resistance.

3. EXPERIMENTAL

3.1 Composition of the Glasses

Twenty four glass samples have been studied. These samples were prepared from four glass compositions. The major ingredient in the glass compositions is the pelletized slag obtained from the National Slag Association in Hamilton, Ontario. The composition of the slag, of the raw mix for the glasses and of the glasses themselves are given in Tables 1, 2 and 3.

Nucleating Agents

Davies and coworkers (J. Iron & Steel Inst., 348-370, April, 1970) used combinations of TiO_2 and chrome ore, and of Fe_2O_3 and carbon successfully as nucleating agents. These combinations have been used with the slag from national Slag Association in this program. Chrome ore was from a high content (48%) Madagascar source.

3.2 Preparation of Glasses

Ball Milling

The chemicals were mixed and milled in ethanol in porcelain ball-mill jars using a borundum medium. The jar was rotated at 0.87 times the critical speed for two hours.

Calcination

The milled raw materials were dried in a drying oven to remove the ethanol. The samples were calcined at 600°C overnight.

TABLE 1

Composition of Slag (wt % and mole %)

Components	SiO_2	Al_2O_3	CaO	MgO	FeO	MnO	$\bar{S}$	TiO_2	Na_2O	K_2O
wt %	38.8	8.0	36.9	12.0	0.7	0.8	1.4	0.4	0.4	0.6
mole %	36.5	4.4	37.3	16.9	0.6	0.6	2.5	0.3	0.4	0.4

TABLE 2

Composition (wt %) of Raw-Mix for Glasses*

Sl.#	Glass Code No.	Slag	Sand	TiO_2	Cr_2O_3	Fe_2O_3	Carbon
1	SC1	73.2	22.0	4.4	0.4	-	-
2	SC2	73.0	21.9	-	-	1.5	3.6
3	SC3	72.0	21.5	-	-	2.9	3.6
4	SC4	70.9	22.3	-	-	4.3	3.5

* TiO_2 and Cr_2O_3 were used as a nucleating mixture for the SC1glass and Fe_2O_3 + carbon were used as a nucleating mixture for the SC2, SC3 and SC4 glasses. The source material for Cr_2O_3 was 48 wt % Cr_2O_3 Madagascar chrome-ore.

TABLE 3

Composition (wt % and mole %) of Glasses*

Glass Code #	SiO_2	Al_2O_3	CaO	MgO	FeO	MnO	$\overline{S}$	TiO_2	Na_2O	K_2O	Cr_2O_3	Fe_2O_3
SC1 wt.%	50.5	5.9	27.0	8.7	0.5	0.6	1.0	4.7	0.3	0.4	0.4	-
SC2 wt.%	52.3	6.0	27.9	9.1	0.5	0.6	1.0	0.3	0.3	0.5	-	1.5
SC3 wt.%	51.4	6.0	27.6	8.9	0.5	0.6	1.0	0.3	0.3	0.4	-	3.0
SC4 wt.%	50.7	5.9	27.1	8.8	0.5	0.6	1.0	0.3	0.3	0.4	-	4.4
SC1 mole %	49.0	3.4	28.1	12.6	0.4	0.5	1.8	3.4	0.3	0.3	0.2	-
SC2 mole %	50.6	3.5	28.8	13.1	0.4	0.5	1.8	0.2	0.3	0.3	-	0.5
SC3 mole %	50.0	3.5	28.9	13.0	0.4	0.5	1.8	0.2	0.3	0.3	-	1.1
SC4 mole %	49.9	3.4	28.7	12.9	0.4	0.5	1.8	0.2	0.3	0.3	-	1.6

* A suffix alphabet associated with the glass code numbers indicates the soak time. For soak times of 3/4, 1, 1-1/2, 2, 3 and 5 hours, the suffixes used are a, b, c, d, e, and f respectively. Thus, e.g.: SC3a, sC3b, SC3c, SC3d, SC3e and SC3f correspond to the samples obtained by melting SC3 glass at 1440°C and soaking for 3/4, 1, 1-1/2, 2, 3, and 5 hours respectively.

Melting and Casting

The SC1, SC2 and SC3 compositions (see Table 3) were melted in Pt-Rh crucibles at a temperature of 1440°C and soaked for 3/4, 1, 2, 3, & 5 hrs. The SC4 glass was melted in a fire-clay crucible, keeping other conditions the same as for other glasses. The melts were cast into bars and were transformed to an annealing furnace at a predetermined annealing temperature. The glasses were melted on a scale of approximately 1300 grams.

3.3 Dilatometric Measurements

The thermal expansion coefficients, the annealing temperatures and the dilatometric softening points of the glasses were measured. These parameters were used to check the uniformity of the glasses from various batches and also to estimate the gradient heat treatment temperature ranges for different glass compositions.

3.4 Nucleation and Crystallization of the Glasses

The glasses were heat treated in a two-stage heating process using the predetermined nucleation and crystallization temperatures. The heat treatment processes were conducted in an isothermal furnace (A4) and in a programmable controlled furnace (Deltech 1).

3.5 X-Ray Diffractometry

The devitrified products were analysed by X-ray diffractometry to identify the crystalline phases. The X-ray powder diffractometer patterns were recorded in the 2θ range 5°-70° using a Philips wide angle goniometer in conjunction with a Philips fully stabilised X-ray generator. Nickel filtered CuK_{α} radiation was used. The "d" spacings and the intensity ratios obtained were compared with standard ASTM patterns. The diffractometer was aligned using a silicon standard.

3.6 Abrasion Testing Apparatus

The abrasion testing apparatus is based on the ASTM 158-72 specifications. The details of the apparatus have been described elsewhere (Final Report No. 67042-81 - "Development of Abrasion Resistant Glass-Ceramics", DSS Contract 052-80-00197). Testing was conducted under the following fixed parameters:

- air pressure - 40 psi
- weight of grits - 35 g
- time of operation - 60 s

The glasses and the corresponding glass-ceramics pertaining to the SC1, SC2, SC3 and SC4 series were cut into rectangular bars (1/4" x 1/2" x 1"). These bars were polished with a series of sand papers having grit sizes 60, 180, 240, 400 and 600. The abrasion test was conducted in duplicate on all the samples.

3.7 Four-Point Bending Tests

The 4-point bending test set-up has been described in detail elsewhere (Final Report No. 67042-81, "Development of Abrasion Resistant Glass-Ceramics", DSS Contract No.OSQ-80-00197).

Test samples were prepared by melting and pouring the glasses into bars (1/4" - 1/2" x 1" x 4-1/2"). The bars were annealed, nucleated and crystallized according to the schedule given in the tables in Section 4.3.

3.8 SEM examination

The fractured glasses and the glass-ceramics obtained from four-point bending tests were subjected to SEM examination. The scanning electron microscope employed is of model SEMCO Nanolab 7. All SEM photomicrographs were taken in the secondary electron mode. The photomicrographs were taken for selected glasses and their corresponding glass-ceramics to compare the morphology of the fractured surfaces.

EDX-ray analysis was also conducted on the fractured surfaces of the SC2f glass and the SC2f glass-ceramic to establish the elemental distribution patterns. The area excited during EDX-ray analysis was 4 mm^2 and EDX-ray resolution was approximately 150 eV at the full width at half maximum.

4. RESULTS AND DISCUSSION

4.1 Dilatometry

The values of the coefficient of linear thermal expansion (CTE) and dilatometric softening point (DSP) for all glasses - SC1, SC2, SC3 and SC4 are given in Table 4. As described in Table 3, the suffixes a, b, c, d, e, & f indicate only the different soak times and not the compositions.

For the samples SC1a, SC2b...SC1f of the SC1 glass obtained by different soak times, the CTE values are very similar except SC1d which has a lower CTE value. The DSP values are identical except for SC1e which has a higher DSP value. The samples obtained from SC2 and SC3 glasses show DSP values that are similar to those observed for the SC1 glasses. In the case of SC4 glass, the samples obtained after 2, 3 & 5 hrs. of soak times i.e. SC4d, SC4e, SC4f show consistently low CTE values. This can possibly be attributed to the combined effect of soak time and slightly higher concentration of Fe_2O_3 in the SC4 glass.

Considering all the CTE and DSP values reported in Table 4, it can be seen that all glasses (SC1, SC2, SC3 and SC4) show similar dilatometric properties: CTE = 8.25×10^{-6} $^{o}C^{-1}$; DSP = 750^{o}C, and presumably because of their almost similar compositions as can be seen from Table 3.

4.2 Controlled Devitrification and Phase Identification

X-ray powder patterns were run for the source slag, for an SC1f sample which was heat treated for 24 hours between 700 and 1009^{o}C in a gradient furnace, and for all the 24 glass-ceramics obtained through nucleation at 720^{o}C for 10 hours and crystallization at 900^{o}C for 3 hours.

In the case of the source slag, the phases detected were akermanite (2 CaO.MgO.2 SiO_2) and merwinite (3 CaO.MgO. 2 SiO_2). The presence of these phases reflects the relative proportions of CaO and MgO in the source slag (see Table 1).

The SC1f glass was heat-treated in a gradient furnace between 700 to 1009^{o}C to establish the nucleation temperature range. The lower temperature limit of 700^{o}C was chosen based on the dilatometric softening point, 750^{o}C. Various thin sections of the heat-treated bar were cut and the nature of the crystals formed in various temperature ranges was determined by X-ray diffractometer. The results are given in Table 5. It can be seen that the crystallization starts in the neighbourhood of the DSP (750^{o}C). The peak patterns observed for all the temperature ranges were similar. The phases identified were fassaite, augite and diopside.

TABLE 4

Coefficient of Linear Thermal Expansion (CTE) and Dilatometric Softening Point (DSP) of Glasses

Glass Name	Thermal Expansion Coefficient ($in/in/^{o}C \times 10^{-6}$)	DSP (^{o}C)
SC1a	8.54	750
SC1b	8.07	750
SC1c	8.23	750
SC1d	7.13	750
SC1e	8.28	775
SC1f	8.31	750
SC2a	8.55	750
SC2b	8.67	750
SC2c	9.54	750
SC2d	8.77	725
SC2e	8.77	750
SC2f	8.06	750
SC3a	8.85	750
SC3b	8.97	750
SC3c	7.86	750
SC3d	8.68	750
SC3e	8.59	750
SC3f	9.09	750
SC4a	8.54	750
SC4b	8.51	750
SC4c	7.80	750
SC4d	6.41	750
SC4e	6.76	775
SC4f	6.78	775

TABLE 5

Phases Detected in the SC1f Bars Heat Treated for 24 Hours Between 700 and 1009°C

Temperature range (°C)	Phases Detected
700 - 706	1) Glass
758 - 763	i) Calcium magnesium
805 - 813	aluminum silicaté (fassaité)
863 - 865	ii) Calcium iron magnesium
950 - 952	silicaté (augité),
1006 - 1009	iii) Calcium magnesium metasilicaté (diopside)

TABLE 6

Phases Detected in SC1, SC2, SC3 and SC4 Series of Glass-Ceramics *

Glass Name	Phases Detected
SC1a SC1b SC1d SC1d SC1e SC1f	
SC2a SC2b SC2c SC2d SC2e SC2f	1) Calcium Iron Magnesium Silicate (Augite), (Ca, Fe, Mg) SiO_3
	2) Calcium Magnesium Meta Silicate (Diopside), $CaMg(SiO_3)_2$
	3) Calcium Iron Magnesium Silicate (Diopside-Hedenbergite) $Ca(Mg_{0.409}Fe_{0.591})(SiO_3)_2$
SC3a SC3b SC3c SC3d SC3f	4) Calcium Magnesium Aluminum Silicate (Aluminum Diopside)(Fassaite) $Ca(Mg_{0.8}Al_{0.2})(Si_{1.8}Al_{0.2})O_6$
SC4a SC4b SC4c SC4d SC4e SC4f	

* The glass-ceramics were prepared by nucleating the glasses at 720°C for 10 hours and crystallizing them at 900°C for 3 hours.

The phases detected in all the 24 glass-ceramics are given in Table 6. The results indicate the presence of pyroxenes (augite, diopside, fassaite) as expected from the chemical composition of the glasses and glass-ceramics given in Table 3.

4.3 Abrasion Resistance

Abrasion measurement results on standard samples, quartzite and alumina, are given in Table 7.

The SC4 was excluded from the abrasion measurements as it had too many occluded bubbles even for the sample soaked for 5 hours. These bubbles are undesirable for a good glass-ceramic product.

Abrasion measurements were carried out on glasses and glass-ceramics of the SC1, SC2 and SC3 series. A total of 24 samples were tested for each series. The abrasion tests were done in duplicate. The results for the 72 measurements are given in Tables 8-14. The data summarized in Table 14 indicate that the glass-ceramic SC2d is the most abrasion resistant.

A comparison of the abrasion resistance of the standard samples with the glasses and glass-ceramics prepared in this project shows that all the glass-ceramics have an abrasion resistance slightly better than that of quartzite, although none show abrasion values comparable to that of alumina.

If abrasion resistance is taken to be directly proportional to hardness and the abrasion resistance of the quartzite is taken to be the same as that of quartz, then the hardness of the glass-ceramics produced here falls between 7 (on MOH's scale for quartz) and 9 (on MOH's scale for corundum) and this is the range of hardness for good glass-ceramics reported in the literature.

TABLE 7

Abrasion Measurement Results on Standard Samples

Glass Comp.	Nucleation Temp. (°C)	Nucleation Time (hr)	Crystallization Temp. (°C)	Crystallization Time (hr)	Colour	Surface Area (cm^2)	Wt of Grit (g)	Wt before (g)	Pressure (psi)	Time (sec)	Wt After (gm)	Wt Loss / Surface Area	Avg. Wt Loss / Surface Area
1) Quartzite	-	-	-	-	Grey	.5024	35	4.7383	40	60	4.7362	.0042	.0041
2)						.5024	35	4.7362	40	60	4.73420	.0040	
1) Alumina	-	-	-	-	white	.5024	35	7.3433	40	60	7.3430	.00067	.0008
2)						.5024	35	7.3430	40	60	7.34250	.0009	

TABLE 8

Heat Treatment and Abrasion Measurement Results

SC1 Glass

Glass Code #	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC)	WT AFTER (GM)	WT LOSS / SURFACE AREA	AVG. WT LOSS / SURFACE AREA
SC1a(i)	Black	.785	35	3.1516	40 psi	60	3.1426	0.0115	0.0110
SC1a(ii)	Black	.5024	35	3.1426	"	60	3.1373	0.0105	
SC1b(i)	Black	.785	35	4.8120	"	60	4.8013	0.0136	0.0128
SC1b(ii)	Black	.5024	35	4.8013	"	60	4.7953	0.0119	
SC1C(i)	Black	.785	35	4.4433	"	60	4.4353	0.0102	0.0096
SC1C(ii)	Black	.5024	35	4.4353	"	60	4.4308	0.0090	
SC1d(i)	Black	.785	35	3.8056	"	60	3.7971	0.0108	0.0109
SC1d(ii)	Black	.5024	35	3.7971	"	60	3.7916	0.0109	
SC1e(i)	Black	.5024	35	2.3633	"	60	2.3569	0.0127	0.0107
SC1e(ii)	Black	.5034	35	2.3569	"	60	2.3526	0.0086	
SC1f(i)	Black	.785	35	4.9639	"	60	4.9559	0.0102	.0097
SC1f(ii)	Black	.5024	35	4.9559	"	60	4.9513	0.0092	

TABLE 9

Heat Treatment and Abrasion Measurement Results

SC1 Glass-Ceramic

Glass Code #	NUCLEATION TEMP. (°C)	NUCLEATION TIME (HR)	CRYSTALLIZATION TEMP. (°C)	CRYSTALLIZATION TIME (HR)	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC.)	WT AFTER (GM)	WT LOSS / SURFACE AREA	AVG. WT LOSS / SURFACE AREA
SC1a(i)	720	10	900	3	Black	.5024	35	3.5888	40	60	3.5873	0.0030	0.0031
SC1a(i)	720	10	900	3	Black	.5024	35	3.5873	"	60	3.5857	0.0032	
SC1b(i)	720	10	900	3	Black	.5024	35	3.7997	"	60	3.7984	0.0026	0.0027
SC1b(i)	720	10	900	3	Black	.5024	35	3.7984	"	60	3.7970	0.0028	
SC1c(i)	720	10	900	3	Black	.5024	35	3.7945	"	60	3.7923	0.0044	0.0029
SC1c(i)	720	10	900	3	Black	.5024	35	3.7923	"	60	3.7916	0.0014	
SC1d(i)	720	10	900	3	Black	.785	35	4.0653	"	60	4.0628	0.0032	0.0030
SC1d(i)	720	10	900	3	Black	.5024	35	4.0628	"	60	4.0614	0.0028	
SC1e(i)	720	10	900	3	Black	.5024	35	4.4779	"	60	4.4766	0.0026	0.0027
SC1e(i)	720	10	900	3	Black	.5024	35	4.4766	"	60	4.4752	0.0028	
SC1f(i)	720	10	900	3	Grey	.5024	35	3.2186	"	60	3.2179	0.0014	0.0020
SC1f(i)	720	10	900	3	Grey	.5024	35	3.2179	"	60	3.2166	0.0026	

TABLE 10

Heat Treatment and Abrasion Measurement Results

SC2 Glass

Glass Code #	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC)	WT AFTER (GM)	WT LOSS / SURFACE AREA	AVG. WT LOSS / SURFACE AREA
SC2a(1	Black	.5024	35	3.9937	40	60	3.9863	.0147	.0135
SC2a(1	Black	.5024	35	3.9863	"	60	3.9801	.0123	
SC2b(1	Black	.5024	35	5.3478	"	60	5.3424	.0107	.0107
SC2b(1	Black	.5024	35	5.3424	"	60	5.3370	.0107	
SC2c(1	Black	.5024	35	3.7441	"	60	3.7390	0.0102	.0104
SC2c(1	Black	.5024	35	3.7390	"	60	3.7337	.0105	
SC2d(1	Black	.5024	35	3.5944	"	3.5886		.0115	.0107
SC2d(1	Black	.5024	35	3.5866	"	60	3.5837	.0098	
SC2e(1	Black	.5024	35	4.2077	"	60	4.2034	.0086	.0098
SC2e(1	Black	.5024	35	4.2034	"	60	4.1979	.0109	
SC2f(1	Black	.5024	35	4.1353	"	60	4.1310	.0086	.0088
SC2f(1	Black	.5024	35	4.1310	"	60	4.1265	.0090	

TABLE 11

Heat Treatment and Abrasion Measurement Results

SC2 Glass Ceramic

Glass Code #	NUCLEATION TEMP. (°C)	NUCLEATION TIME (HR)	CRYSTALLIZATION TEMP. (°C)	CRYSTALLIZATION TIME (HR)	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC)	WT AFTER (GM)	WT LOSS / SURFACE AREA	AVG. WT LOSS / SURFACE AREA
SC2a(i	720	10	900	3	Black	.5024	35	3.2130	40	60	3.2112	0.0036	0.0042
SC2a(i	720	10	900	3	Black	.5024	35	3.2112	"	60	3.2088	0.0048	
SC2b(i	720	10	900	3	Black	.5024	35	3.8694	"	60	3.3680	0.0028	0.0023
SC2b(i	720	10	900	3	Black	.5024	35	3.8680	"	60	3.8671	0.0018	
SC2c(i	720	10	900	3	Black	.5024	35	3.3953	"	60	3.3940	0.0026	0.0030
SC2c(i	720	10	900	3	Black	.5024	35	3.3940	"	60	3.3923	0.0034	
SC2d(i	720	10	900	3	Black	.5024	35	3.6294	"	60	3.6289	0.0010	0.0012
SC2d(i	720	10	900	3	Black	.5024	35	3.6289	"	60	3.6282	.0014	
SC2e(i	720	10	900	3	Black	.5024	35	2.8407	"	60	2.8492	0.0030	0.0039
SC2e(i	720	10	900	3	Black	.5024	35	2.8492	"	60	2.8468	0.0048	
SC2f(i	720	10	900	3	Black	.5024	35	3.1253	"	60	3.1240	0.0026	0.0023
SC2f(i	720	10	900	3	Black	.5024	35	3.1240	"	60	3.1230	0.0020	

TABLE 12

Heat Treatment and Abrasion Measurement Results

SC3 Glass

Glass Code #	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC)	WT AFTER (GM)	WT LOSS / SURFACE AREA	AVG. WT LOSS / SURFACE AREA
SC3a(i)	Black	.5024	35	4.0659	40	60	4.0610	0.0098	0.0099
SC3a(ii)	Black	.5024	35	4.0610	"	60	4.0560	0.0100	
SC3b(i)	Black	.5024	35	3.7168	"	60	3.7122	0.0092	0.0094
SC3b(ii)	Black	.5024	35	3.7122	"	60	3.7074	0.0096	
SC3c(i)	Black	.5024	35	3.4116	"	60	3.4060	0.0111	0.0104
SC3c(ii)	Black	.5024	35	3.4060	"	60	3.4012	0.0096	
SC3d(i)	Black	.5024	35	4.4694	"	60	4.4648	0.0092	0.0079
SC3d(ii)	Black	.5024	35	4.4648	"	60	4.4615	0.0066	
SC3e(i)	Black	.5024	35	4.7012	"	60	4.6950	0.0123	0.0108
SC3e(ii)	Black	.5024	35	4.6950	"	60	4.6904	0.0092	
SC3f(i)	Black	.5024	35	1.7640	"	60	1.7591	0.0098	0.0096
SC3f(ii)	Black	.5024	35	1.7491	"	60	1.7544	0.0094	

TABLE 13

Heat Treatment and Abrasion Measurement Results

SC3 Glass-Ceramic

Glass Code #	NUCLEATION TEMP. (°C)	NUCLEATION TIME (HR)	CRYSTALLIZATION TEMP. (°C)	CRYSTALLIZATION TIME (HR)	RESULTS	SURFACE AREA (CM^2)	WT OF GRIT (GM)	WT BEFORE (GM)	PRESSURE (PSI)	TIME (SEC)	WT AFTER (GM)	WT LOSS SURFACE AREA	AVG. WT LOSS SURFACE AREA
SC3a(i)	720	10	900	3	Black	.5024	35	2.5663	40	60	2.5658	0.0010	0.0028
SC3a(ii)	720	10	900	3	Black	.5024	35	2.5658	"	60	2.5635	0.0046	
SC3b(i)	720	10	900	3	Black	.5024	35	3.0368	"	60	3.0359	0.0018	0.0031
SC3b(ii)	720	10	900	3	Black	.5024	35	3.0359	"	60	3.0337	0.0044	
SC3c(i)	720	10	900	3	Black	.5024	35	2.7319	"	60	2.7305	0.0028	0.0039
SC3c(ii)	720	10	900	3	Black	.5024	35	2.7305	"	60	2.7280	0.0050	
SC3d(i)	720	10	900	3	Black	.5024	35	1.8695	"	60	1.8678	0.0034	0.0041
SC3d(ii)	720	10	900	3	Black	.5024	35	1.8678	"	60	1.8654	0.0048	
SC3e(i)	720	10	900	3	Green Outside	.5024	35	3.4851	"	60	3.4836	0.0030	0.0027
SC3e(ii)	720	10	900	3	Black Inside	.5024	35	3.4836	"	60	3.4824	0.0024	
SC3f(i)	720	10	900	3	"	.5024	35	2.7736	"	60	2.7728	0.0016	0.0028
SC3f(ii)	720	10	900	3	"	.5024	35	2.7728	"	60	2.7708	0.0040	

TABLE 14

Abrasion Tests on Glasses and Glass-Ceramics

Code No.	Glass Average Wt. Loss per Unit Area ($g.cm^{-2}$)	Glass-Ceramics Average Wt. Loss per Unit Area ($g.\ cm^{-2}$)	Wt. Loss per Unit Area for Glass / Wt. Loss per Unit Area for glass-ceramic
SC1a	0.0110	0.0031	3.55
SC1b	0.0128	0.0027	4.74
SC1c	0.0096	0.0029	3.31
SC1d	0.0109	0.0030	3.63
SC1e	0.0107	0.0027	3.96
SC1f	0.0097	0.0020	4.85
SC2a	0.0135	0.0042	3.21
SC2b	0.0107	0.0023	4.65
SC2c	0.0104	0.0030	3.46
SC2d	0.0107	0.0012	8.91
SC2e	0.0098	0.0039	2.51
SC2f	0.0088	0.0023	3.83
SC3a	0.0099	0.0028	3.54
SC3b	0.0094	0.0031	3.03
SC3c	0.0104	0.0039	2.67
SC3d	0.0079	0.0041	1.92
SC3e	0.0108	0.0027	4.00
SC3f	0.0096	0.0028	3.43

4.4 Modulus of Rupture

In view of the abrasion test results, samples corresponding to Code nos. SC1b, SC1d, SC1f based on the TiO_2 + Cr_2O_3 nucleating agent mixture; and SC2b, SC2d and SC2f based on the Fe_2O_3 + carbon nucleating agent mixture were selected for four point bending tests.

The test results, along with heat-treatment, are given in Table 15. The ratio of modulus of rupture (MOR) for glass-ceramics and glasses is given in Table 16.

The highest MOR value, 7963 psi, was observed for composition SC2f (glass-ceramic).

In general, it was found that the MOR values were low compared with those found for most glasses (about 70 $MN.m^{-2}$ or $\sim$ 10,000 psi) and glass-ceramics (200-280 $MN.m^{-2}$ or $\sim$ 30,000 - 40,000 psi). It is concluded that the glass-ceramics of the SC1 and SC2 series investigated in this project have good abrasion resistance but are lacking in strength. The abrasion resistant glass-ceramics in the MgO-CaO-Al_2O_3-SiO_2 systems prepared under the aforementioned contract (Development of Abrasion Resistant glass-ceramics) had higher strength (51 - 120 $MN.m^{-2}$ or 7,400 - 17,400 psi) but lower abrasion resistance. It should be noted that those glass-ceramics were higher in Al_2O_3 ($\sim$ 10-25%) and lower in CaO (10-25%) than the glass-ceramics prepared in this project (Al_2O_3 $\sim$ 5%, CaO $\sim$ 28%).

TABLE 15

Moduli of Rupture of Glasses & Glass-Ceramics
by the 4-Point Bending Method

Glass Code No.		Nucleation		Crystallization		Width	Thickness	Modulus of Rupture (psi)	
		Temperature (°C)	Time (hrs)	Temperature (°C)	Time (hrs)	(in)	(in)		
SC 1b(g)	1.	-	-	-	-	.9570	.3990	4509	3523
	2.	-	-	-	-	.9655	.3990	2537	
SC 1b(gc)	1.	720	10	900	3	1.0225	.4620	3326	2748
	2.	720	10	900	3	.9840	.4190	2170	
SC 1d(g)	1.	-	-	-	-	1.0448	.4710	4167	4991
	2.	-	-	-	-	.9382	.4330	5815	
SC 1d(gc)	1.	720	10	900	3	.9730	.4012	5363	5584
	2.	720	10	900	3	1.0510	.4160	5805	
SC 1f(g)	1.	-	-	-	-	.9923	.4940	3493	3778
	2.	-	-	-	-	.9405	.4885	4063	
SC 1f(gc)	1.	720	10	900	3	.9052	.4900	4389	4277
	2.	720	10	900	3	1.0468	.4750	4166	
SC 2b(g)	1.	-	-	-	-	1.0140	.4185	2905	4060
	2.	-	-	-	-	.994	.3750	5215	
SC 2b(gc)	1.	720	10	900	3	1.0890	.4738	994	1199
	2.	720	10	900	3	.9985	.4240	1404	
SC 2d(g)	1.	-	-	-	-	1.3350	.4422	2758	2965
	2.	-	-	-	-	.9810	.4380	3172	
SC 2d(gc)	1.	720	10	900	3	1.0500	.4480	4057	2749
	2.	720	10	900	3	.9730	.4760	1442	
SC 2f(g)	1.	-	-	-	-	.9670	.3921	3892	3499
	2.	-	-	-	-	.9940	.4275	3104	
SC 2f(gc)	1.	720	10	900	3	1.0920	.3890	9603	7963
	2.	720	10	900	3	.9650	.4130	6324	

TABLE 16

Moduli of Rupture of Glasses and Glass-Ceramics

Glass Code No.	Glass		Glass-Ceramics		Modulus of Rupture Ratio
	Modulus of Rupture (psi)	($MN.m^{-2}$)	Modulus of Rupture (psi)	($MN.m^{-2}$)	
SC 1b	3523	24.34	2748	18.98	0.7800
SC 1d	4991	34.48	5584	38.58	1.1188
SC 1f	3778	26.10	4277	29.55	1.1320
SC 2b	4060	28.05	1199	8.28	0.2953
SC 2d	2965	20.48	2749	18.99	0.9271
SC 2f	3499	24.17	7963	55.02	2.2757

4.5 Optical Microscopy

Optical micrographs of selected samples - SC1b, SC2b and SC2f (both glass and glass-cermaic) were taken with a Nikon Microscope Model CL. All photomicrographs were taken at a magnification of 370. The surfaces photographed were those obtained after fracturing of the sample on a 4-point bending test unit.

Figure 1 shows that the SC1b glass surface is smooth but that the glass-ceramic has coarse clinopyroxene spherulites. Figures 2 and 3 show similar features.

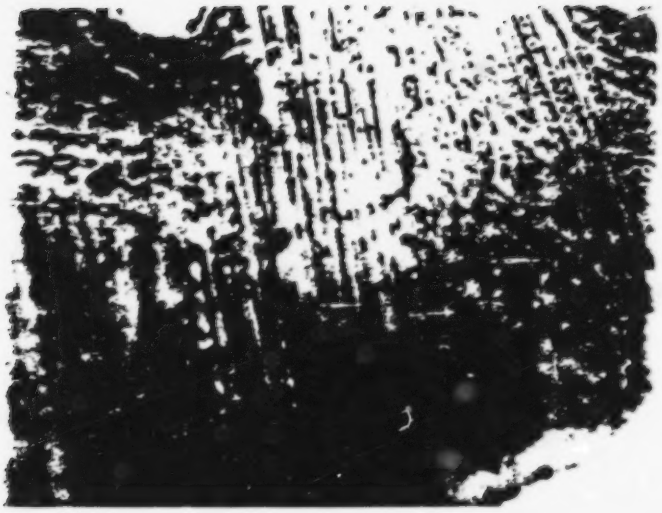
By and large, the glass-ceramic photographs show that the products do not have a very fine grained structure as is generally reported in the literature. The fine grained glass-ceramic structure obtained using a Fe_2O_3 + carbon mixture as a nucleating agent depends on the melt. The Fe^{2+}/Fe^{3+} ratio in the melt can be varied by using an oxidising agent [$NH_4(NO_3)$] or a reducing agent (carbon).

4.6 SEM Analysis

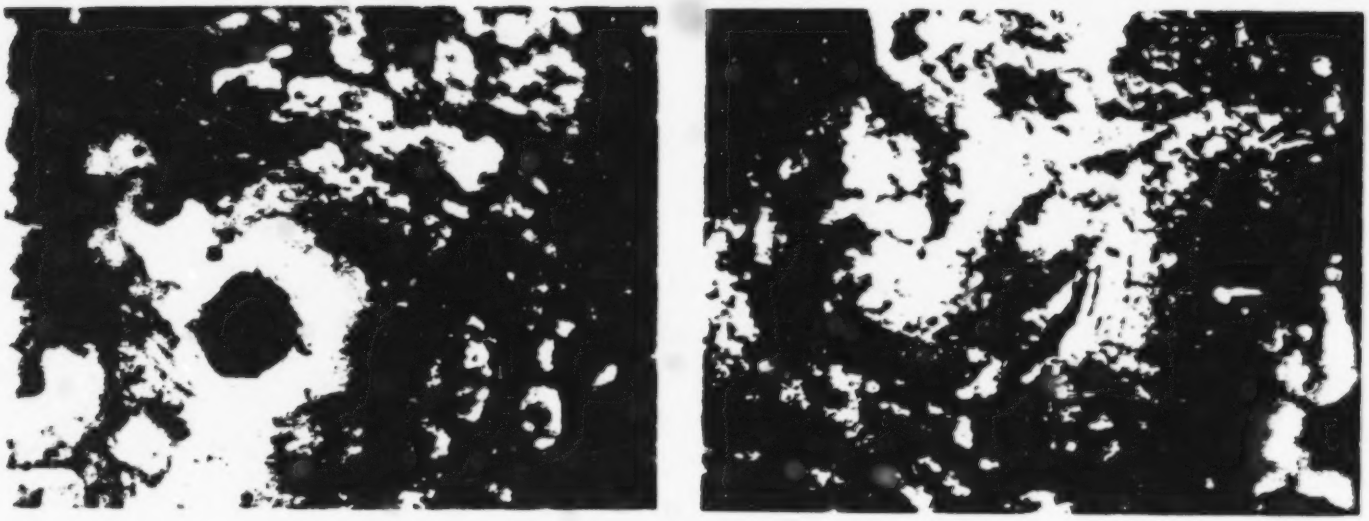
SEM photomicrographs and EDX-ray spectra were obtained to compile information concerning the microstructure of the glasses and the glass-ceramics.

SEM Photomicrographs

Figure 5 and Figure 6 (a & b) show electron micrographs of the fracture surfaces of SC1b glass. These micrographs show that the surface is smooth and homogeneous with some porosity and some shrinkage porosity, cavities and conchoidal fracture of a smooth glass.



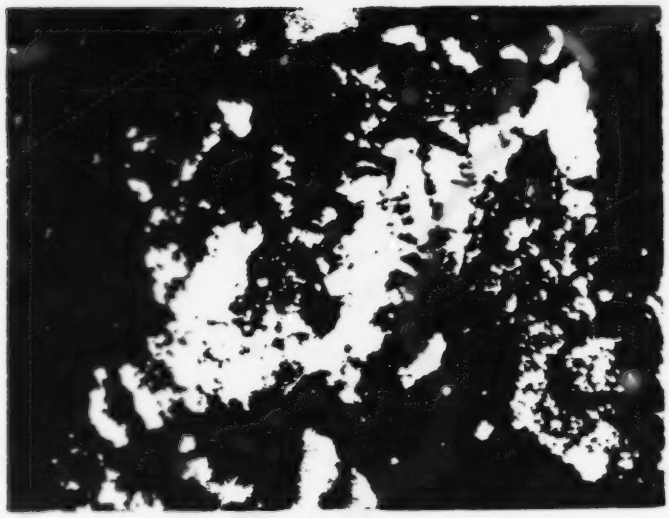
(a)



(b)

FIGURE 1: Optical micrographs of fracture surfaces of SC1b (a) Glass, and (b) Glass-Ceramics

(a)



(b)

FIGURE 2: Optical micrographs of fracture surfaces of SC2b (a) glass [illegible] glass-ceramic

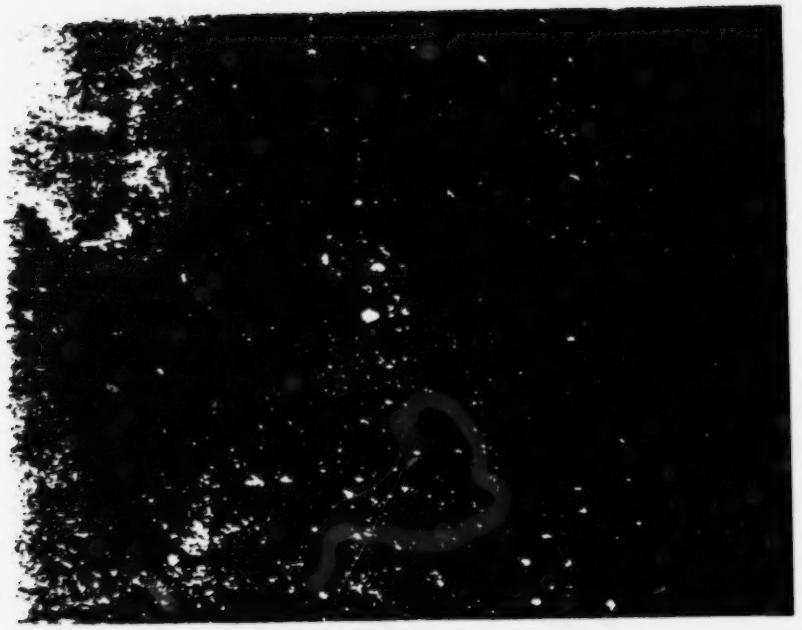
Abrasive wear can also occur when a third particle harder than one or both of the surfaces in contact with each other is trapped in the interface. This particle can remove the material from one or both surfaces.

A third type of abrasive wear can result from the impingement of finely divided solids, such as silicon carbide, that are suspended in the surrounding medium of the ceramic (air, gas or liquid).

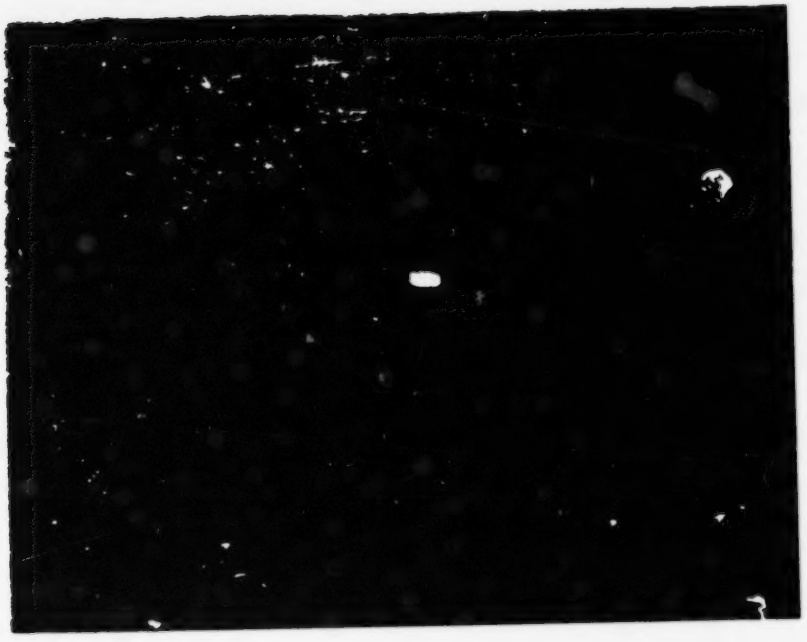
6.2 Abrasion Resistance

The degree of abrasion-resistance of a material depends upon the grain size, hardness, shape, weight and the operating conditions, such as the atmosphere, the prevailing temperature, etc. McMillan[1] suggested that the abrasion resistance of a material under closely specified conditions may be taken as one measure of its hardness. Using Moh's scale glass-ceramics may reach hardness approximating those of corundum (Al_2O_3) and silicon carbide which are in the 9-9.5 range. Glass-ceramics may reach hardness, considerably greater than those of glasses which are usually between 5 and 7.

Besides the scratch test associated with Moh's scale indentation hardness techniques such as the Knoop hardness test, the diamond pyramid hardness test (D.P.H.) and the Rockwell test can be applied although none of these methods can be regarded as truly satisfactory for measuring the hardness of non-ductile materials such as glass-ceramics.



(a)



(b)

FIGURE 4: Electron micrographs of fracture surface of SC1b Glass at Different Magnifications

FIGURE 5: Electron Micrograph of fracture surface of SCl5 glass at different magnification

(a)

(b)

FIGURE 6: Electron micrographs of fracture surface of SC1b glass from an other region

Figure 7 shows the electron micrographs of the fracture surfaces of the SC1b glass-ceramics. The micrographs show the conchoidal fracture pits of an irregular feature, and fine particulate materials across the whole fracture surface.

Figure 8 shows the electron micrographs of fracture surfaces of the SC2b glass. The fracture on the edge is smooth. There are pits, porosity and a few inclusions.

Figure 9 shows the electron micrographs of the fracture surfaces of the SC2b glass-ceramic. The presence of conchoidal fracture, linked structures of domed appearance is evident. The (a) photomicrograph shows the fracture of one dome structure.

Figure 10 shows the electron micrographs of the fracture surfaces of SC2f glass. The micrographs show the general smooth appearance of the surface with some porosity.

Figure 11 shows the electron micrographs of the fracture surfaces of SC2f glass-ceramics. The surface roughness is less. There is a fine grained structure with a chain of porosity. The fracture mode is conchoidal but of lesser size.

Figure 12, 13 & 14 show the electron micrographs of SC2f glass-ceramic at higher magnifications.

Figure 13(b) and 14 show micrographs obtained for the etched surface of the specimen. The sample was first polished to 1μm finish and subsequently etched in a 3% solution of HF for 30 seconds.

Intergranular failure generally increased with test temperatures, grain boundary impurities and porosity. Since these factors also generally lower the strength, and increase in intergranular failure may indicate a reduction in the strength of the glass-ceramic. Negro and Bachiorrini[36] found that the fracture surface of glass-ceramics is essentially trans-crystalline with river cleavages. It was found that CaO increases the grain size, Al_2O_3 raises the brittleness, SiO_2 enhances the fracture propagation and MgO improves the devitrification.

7.3 Methods of Testing the Strength of Glass

The strength of a glass or a glass-ceramic, and its resistance to fracture can be investigated by bending a glass beam. A beam under load at one surface has tensile stress on one side and compressive stress on the other. Maximum stress occurs at the surface. In three point bending (Figure 6) the maximum tensile stress occurs at the central load point. In four point bending (Figure 7), the whole loading surface experiences the same maximum tensile stress. Therefore, four point bending produces a result which is more representative for the material as a whole than three point bending.

Provided that the spacing of the loading point is large compared with the depth of the beam and that the deflection of the beam is small, the maximum tensile surface stress is given by:

$$\sigma_{max} = \frac{M}{D}$$

where M is the maximum bending movement

$$M = \frac{La}{2}$$

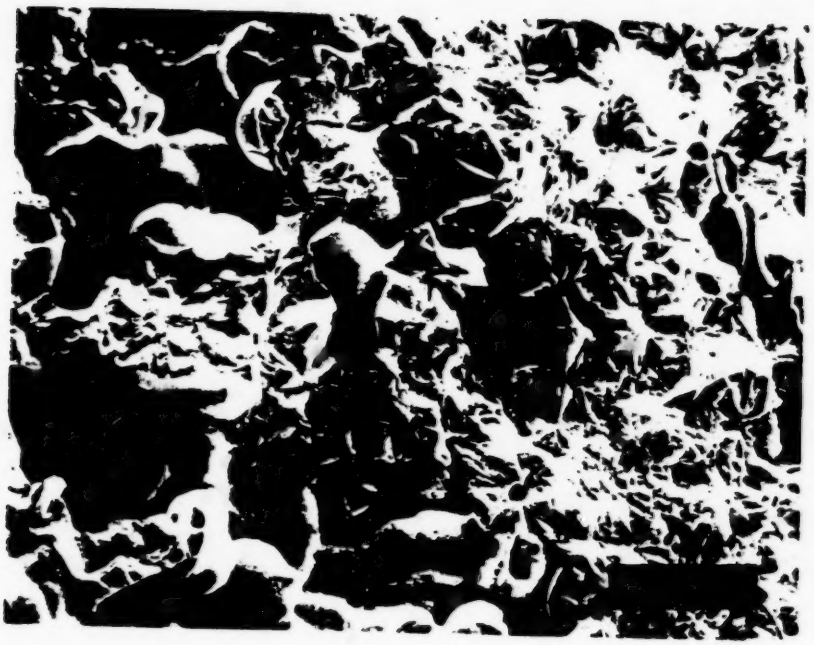
and D depends on the dimension and the cross-section of the beam $D = \frac{1}{4}\pi r^3$ for circular cross-section, for rectangular $D = \frac{1}{6}$ width x (depth)^2.

(a)

(b)

FIGURE 8: Electron micrographs of fracture surface of SC2b glass

(a)



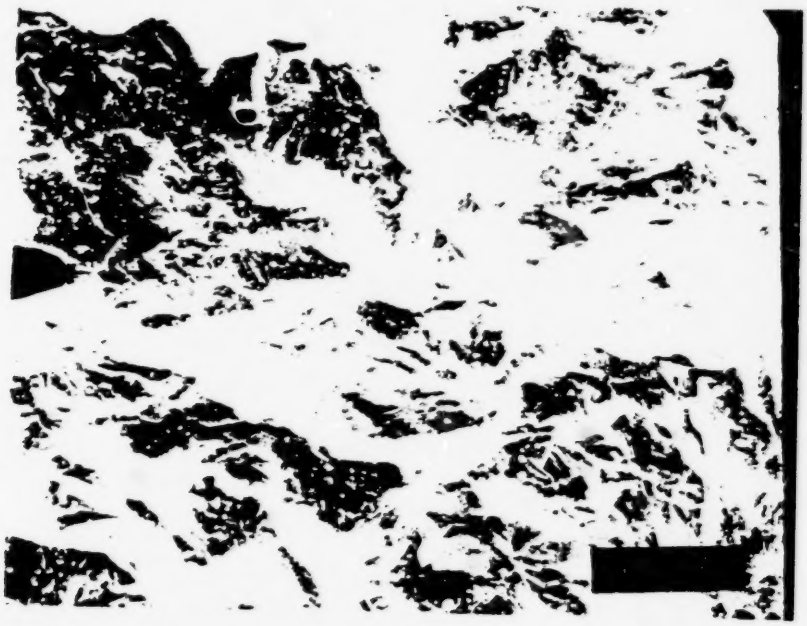
(b)

FIGURE 9: Electron micrographs of fracture surface of SC2b glass-ceramics

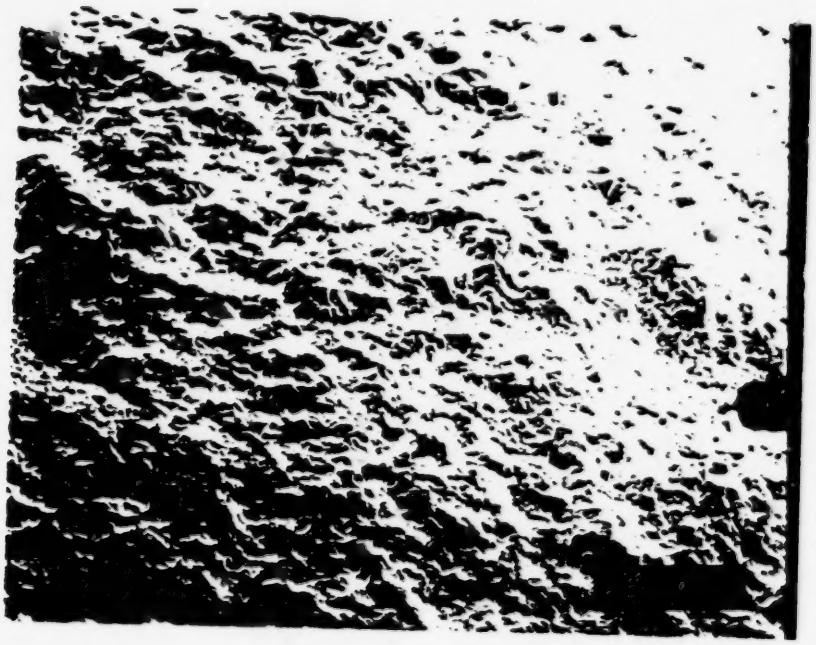
(a)

(b)

FIGURE 10: Electron micrographs of fracture surface of SC2f glass



(a)



(b)

FIGURE 11: Electron micrographs of fracture surface of SC2f glass-ceramics

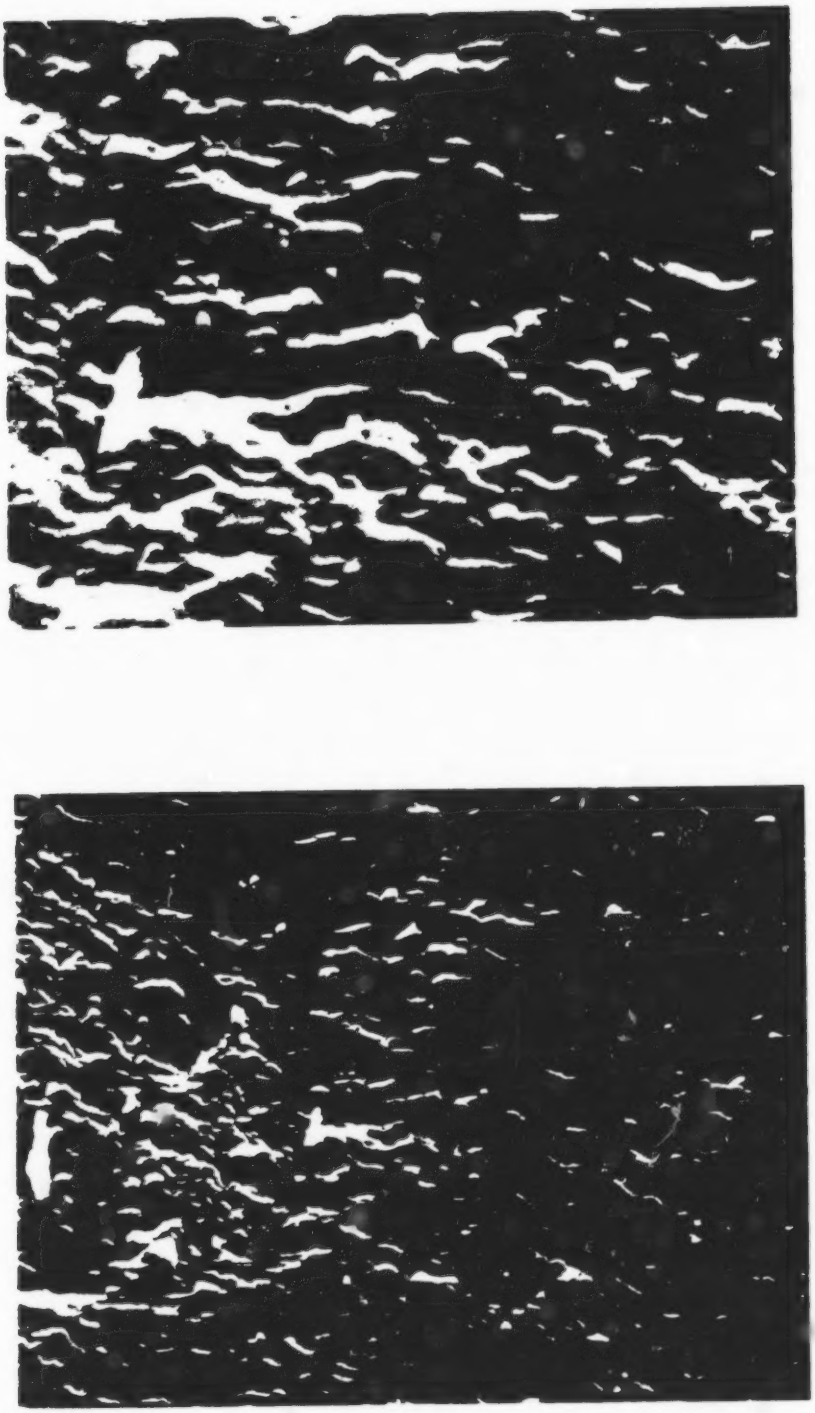
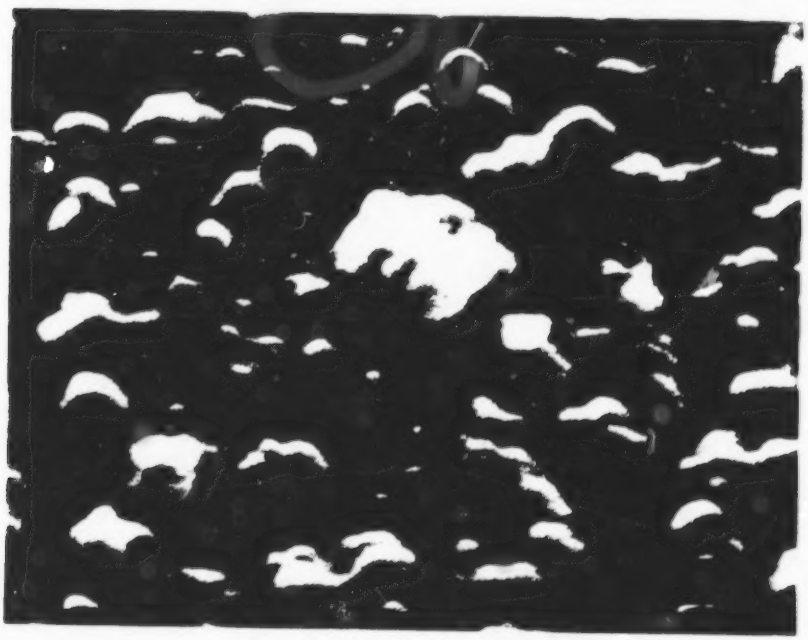


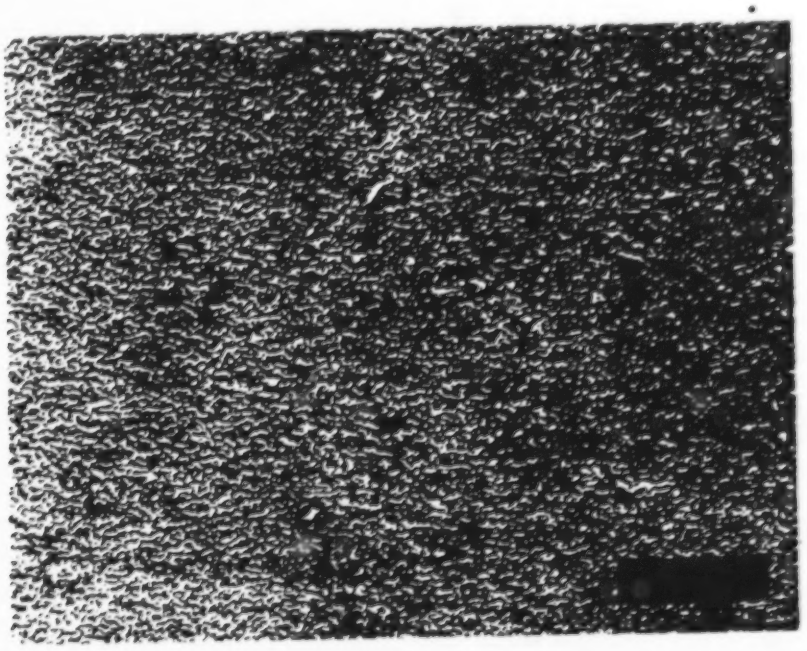
FIGURE 12: Electron micrographs of fracturer surface of SC2f glass-ceramic

(a)

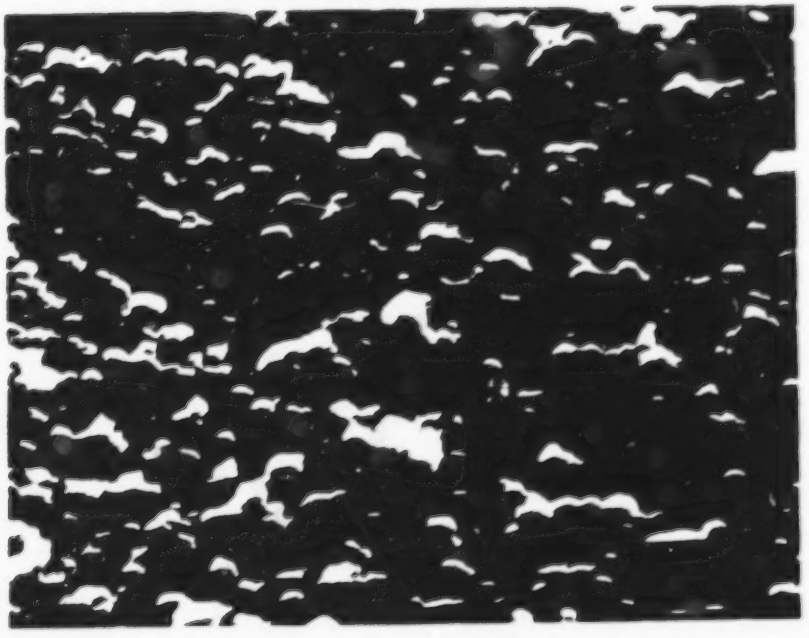


(b)

FIGURE 13: Electron micrographs of fractured surface of SC2f glass-ceramic. (a) without etching (b) after etching



(a)



(b)

FIGURE 14: Electron micrographs of fractured surface after etching

The micrographs of the etched surface show that the large area is occupied by the nodule structures. However, these nodules are not so uniformly distributed as generally seen in the case of a good glass-ceramics (page 14, Appendix A). By comparing the micrographs given in Figures 13(b) and 14(b), it can be seen that due to the difference in the magnification, there is no apparent difference in the surface feature and, therefore, the micrographs were not taken at still higher magnification.

To get the uniform nucleation, the maximum amount of Fe_3O_4 is required to be formed. To get the maximum amount of Fe_3O_4, the FeO/Fe_2O_3 mole ratio should be 1. This mole ratio is varied by adding oxidising or reducing agents in the melt. During the present study, the Fe^{2+}/Fe^{3+} ratio was not optimum.

In view of the above, non uniform nucleation and relatively coarse grained structures of the glass-ceramics were responsible for the low mechanical strength described in the preceding section. The relationship between abrasion resistance and the microstructure, however, is not well defined in the literature.

EDX-Ray Spectra

Figure 15 shows the EDX-ray spectra of SC2f glass. Two spectra were taken from two different regions to check the homogeneity. The two superimposed spectra show that the pattern of elemental distributions at the two different regions are almost the same, and therefore, the glass is homogeneous. As the sample was coated with gold to make the surface conductive, Au is shown to be present in the sample. These spectra also show the high concentration of silicon and calcium as evident from the composition of the glass given in Table 3.

FIGURE 15

E.D. X-Ray Spectra

Job Number 83555 Date March 29/83

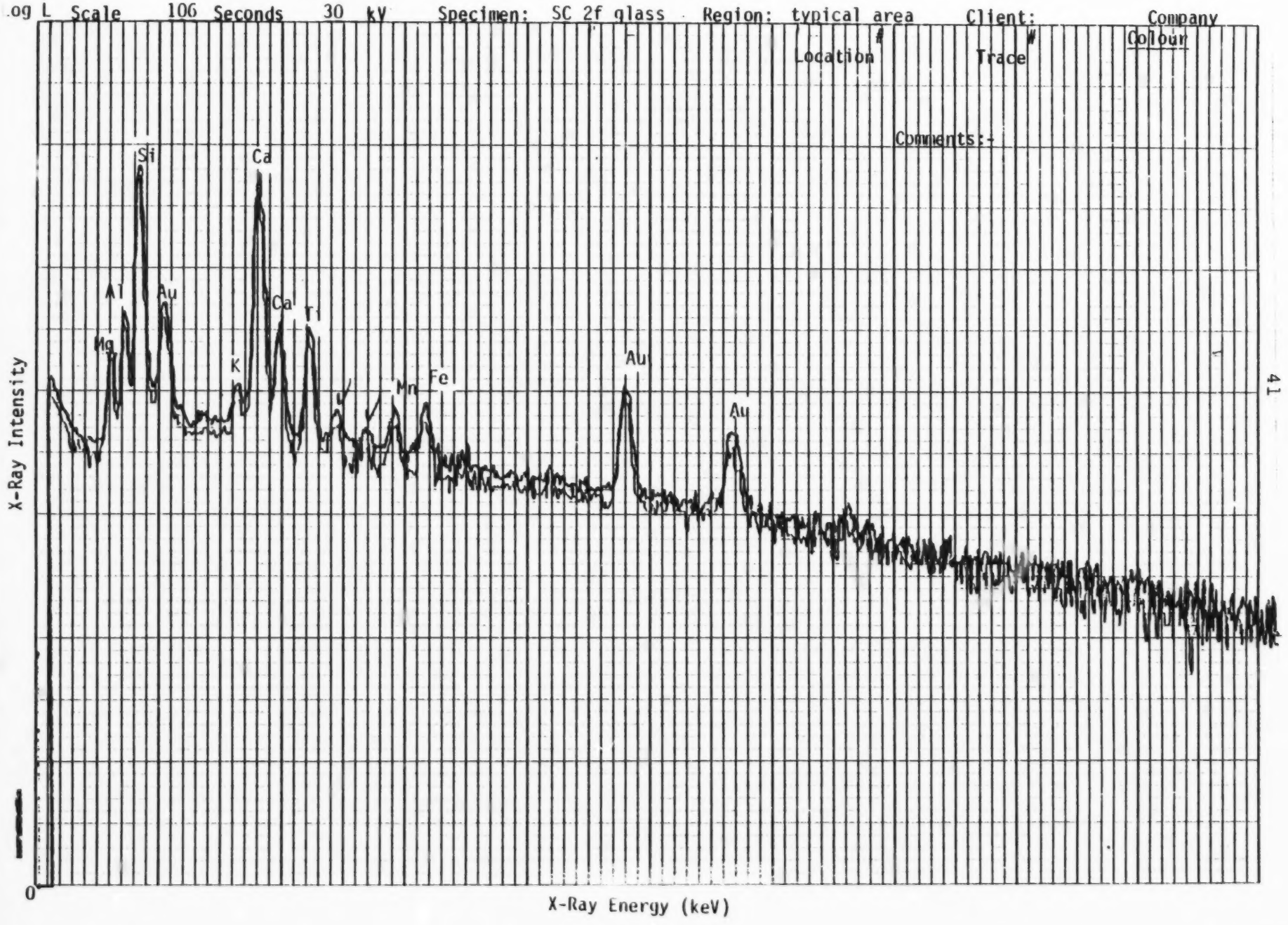


FIGURE 16

E.D. X-Ray Spectra Job Number 83555 Date March 29/83

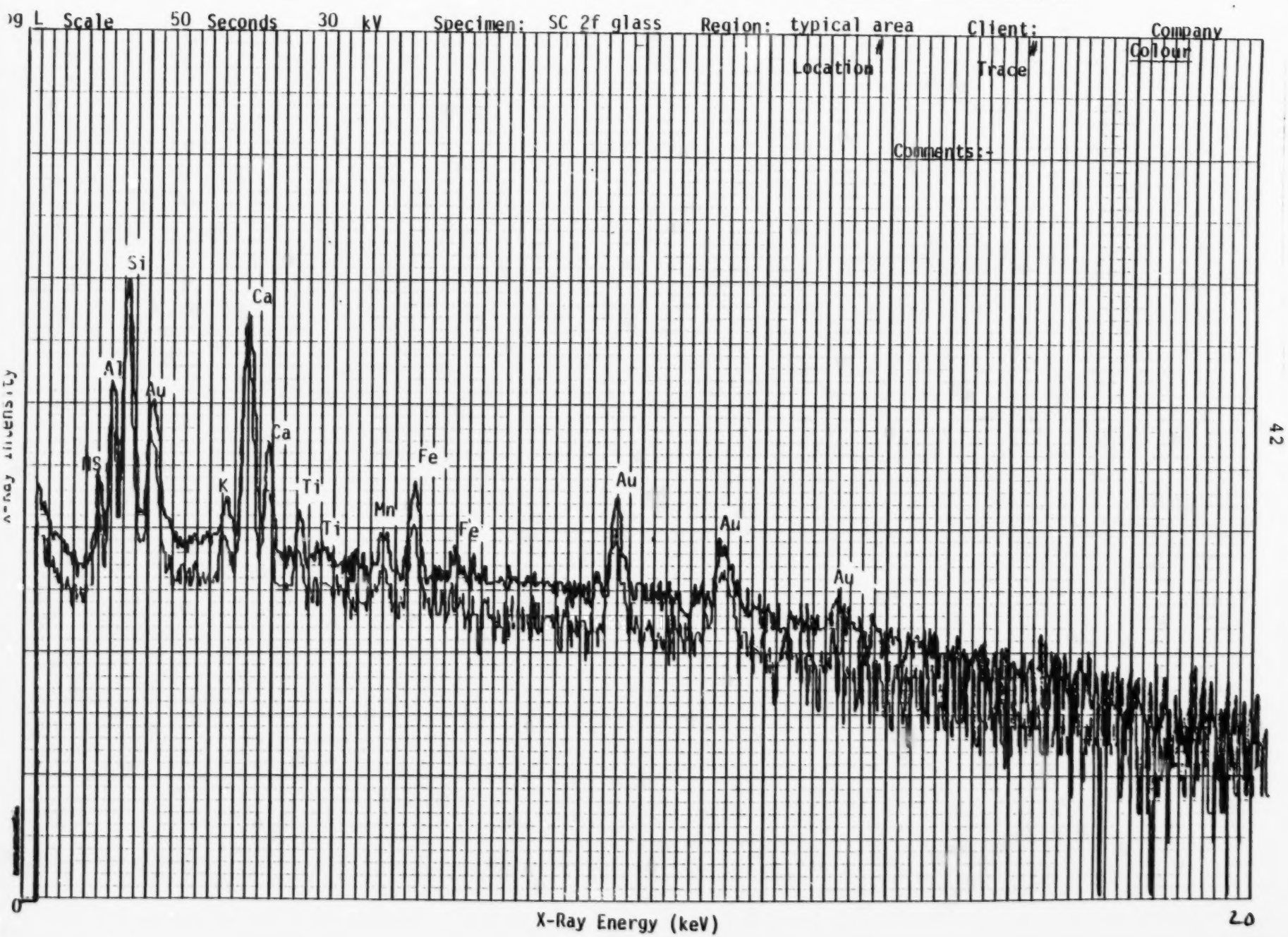


Figure 16 shows the EDX-ray spectra of the SC2f glass-ceramics. The spectra show identical features as described for the glass indicating that the glass-ceramics are homogeneous when the elemental distribution is measured in the $4mm^2$ area, excited by the electron beam to emit the characteristic x-rays.

5. CONCLUSIONS AND RECOMMENDATIONS

The glass ceramics developed during the present work have good abrasion resistance. The abrasion resistance lies between that of quartzite (hardness: 7 moh) and corundum (hardness:9 moh).

The strength of the glass-ceramics as measured in terms of modulus of rupture lies between $8MN.m^{-2}$ and $55\ MN.m^{-2}$.

In order to produce commercially viable glass-ceramic materials from the blast furnace slags investigated in this program, it is recommended that:

i) The strength and abrasion resistance of the glass-ceramic material be improved through modifying the heat-treatment schedule and possibly by adding minor quantities of alumina.

(ii) The duration of heat-treatment cycle, if possible, be reduced to make the process more energy efficient.

(iii) The relationship between the nucleating agent (Fe^{++}/Fe^{+++}) and the microstructure of the glass-ceramics be investigated further.

6. ACKNOWLEDGEMENT

We gratefully acknowledge the assistance of Mrs. S. Hemraj for her

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Deputy Manager
Glass & Ceramics Technology Centre

APPENDIX A

LITERATURE SURVEY ON SLAG-CERAMICS

1. INTRODUCTION

Glass-ceramics are known to have a higher mechanical strength and a greater abrasion resistance than the parent glasses.

Among the various kinds of glass-ceramics, the slag-ceramics have been found to have excellent abrasion resistance.

Slag being a waste product is reasonably cheap and, therefore, the slag-ceramics can be economically produced by the building-materials industry for the construction of floor tiles, spouts, pipelines, and bases subject to abrasion.

In view of the various applications of the slag-ceramics, there is a substantial amount of research and development work on these materials. In this appendix, a brief description of the current trends in the development of glass-ceramics from slags is given.

2. COMPOSITION OF SLAGS

The chemical composition of a slag depends on the particular process by which it is produced. A few slag compositions which have been used to form glass-ceramics, are given below in Table 1.

TABLE 1 (Reference No. 1)

Composition of Slags used to make Slag-ceram, (wt-%)

	SiO_2	Al_2O_3	CaO	MgO	FeO	MnO	S^{2-}	Total S	Total Fe	CaO/SiO_2
Slag *A*	31·3	17·9	37·9	7·1	0·64	0·59	0·92	1·60	0·75	1·21
Slag *B*	35·8	18·9	32·2	6·9	1·06	0·40	1·49	1·80	1·58	0·90
Slag *C*	32·3	17·5	41·6	5·0	0·89	1·14	0·87	1·03	1·37	1·29
Slag *D*	30·4	15·5	42·8	5·9	0·73	0·94	0·63	0·95	1·01	1·41
Slag *E*	38·0	21·0	nd	35·0*	1·1	nd	nd	nd	nd	nd

* this figure represents CaO+MgO, but the majority is MgO; Slag *E* also contains about 4%Cr_2O_3

The analysis of Slag E, is incomplete because its composition is very different from other slag compositions given in the Table 1. The slags-A, B, C & D come from a blast furnace but Slag E comes from a ferro-chrome smelter.

Open-hearth slags from the Bezhitskii Steel Smelting Works (2) and electrofurnace slags from the Bezhitskii Steel Casting Plant (3) have been successfully used to develop pyroxenic glass-ceramics. The compositions of the slags are given in Table 2.

TABLE 2 (Reference No. 1, 2)

Slag Compositions (wt-%) used In the Soviet Union

Name of Slags	SiO_2	MnO	Al_2O_3	FeO	TiO_2	CaO	MgO	NaO_2	K_2O	Cr_2O_3	$\overline{S}$	Fe_2O_3
Open Hearth Slag	31.88	7.66	3.96	10.77	0.33	27.91	17.07	0.25	0.12	1.37	0.17	-
Electric Furnace Slag	51.40	13.20	5.42	9.0	0.22	10.96	5.82	0.45	0.26	0.86	0.27	21.3

3. COMPOSITION OF SLAG-GLASS-CERAMICS

The composition of slag is modified to synthesize a pyroxene composition in the SiO_2-CaO-MgO system. The pyroxenes have a distinctly high crystallization tendency and provide better physicochemical and mechanical properties in the crystalline products. The tendency of pyroxenes for a broad isomorphism makes it possible for different cations to be incorporated into the crystal lattice.

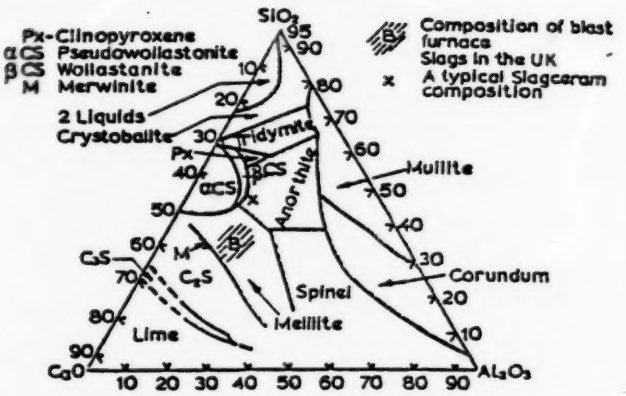

Figure 1: The section MgO=5% of the liquidus diagram for the system $CaO-Al_2O_3-MgO-SiO_2$ (after Cavalier and Sandrea-Deudon and Majumdar) (Reference No. 1)

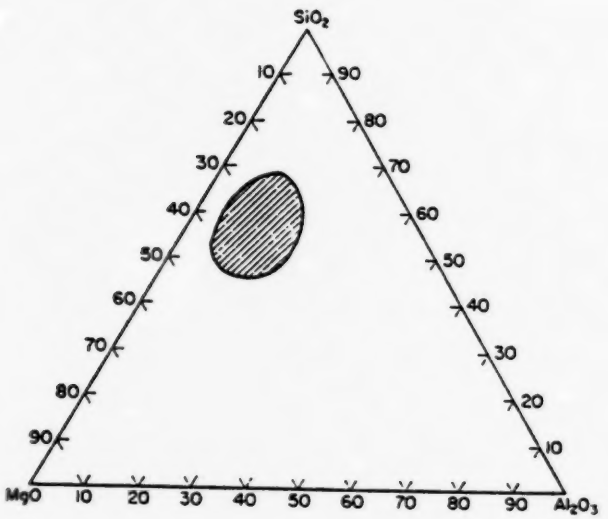

Figure 2: Region of glass formation in the $MgO-Al_2O_3-SiO_2$ system (molecular percentage composition) (Reference No. 4)

The phase diagram for $CaO-Al_2O_3-MgO-SiO_2$ is given in Figure 1.

From this Figure 1, it is evident that additional SiO_2 is required to modify the slag composition to bring it in the vicinity of clinopyroxene.

It is also important to note that the modified compositions are those which fall in the region of glass formation shown in Figure 2 for the $MgO-SiO_2-Al_2O_3$ sytem. The same region applies to the MgO (CaO) $-SiO_2-Al_2O_3$ system.

The compositions of Px and U.K. slags as represented in Figure 1 and the centre of glass forming region in Figure 2 are given in Table 3 for comparison purpose.

TABLE 3

Composition (mole%)

	SiO_2	Al_2O_3	CaO	MgO
Px	60	11	24	5
UK. Slag	37	21	37	5
Glass Forming Region	56	14	-	30

4. PREPARATION AND PROPERTIES OF SLAG GLASS-CERAMICS

In the development of glass-ceramics, the nucleation and crystallization temperatures are fixed in accordance with the nucleation and crystallization rate curves proposed by Tamman (5) (Figure 3).

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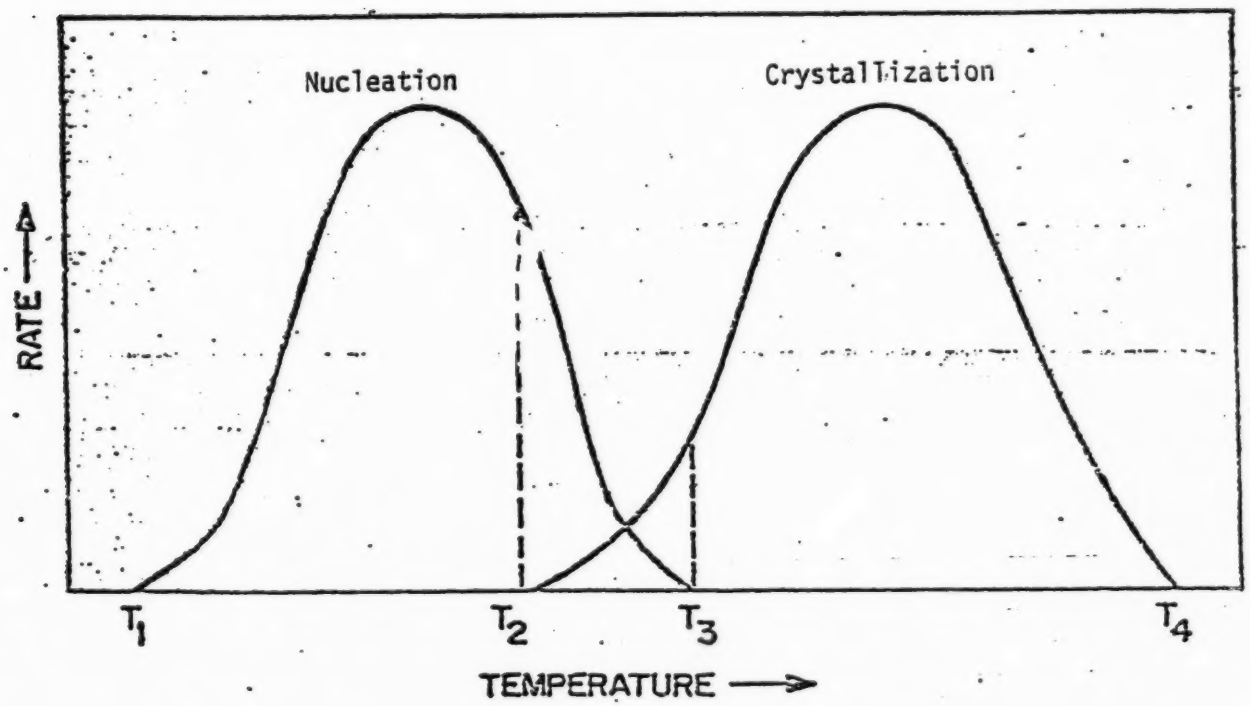

Figure 3: Nucleation and Crystallization Rate Curves (Reference No.5)

T_1 and T_3: Minimum and maximum nucleation temperatures

T_2 and T_4: Minimum and maximum crystallization temperatures

The controlled devitrification is achieved by holding a glass sample first at a temperature in the nucleation region, subsequently raising the temperature and holding the sample in the temperature range of crystallization.

For small crystal sizes, the maximum nucleation rate combined with a moderate (not maximum) crystal growth rate is preferred. If the shortest possible heat-treatment time is desired and no other conditions are laid down, then maximum rates for both steps are desirable.

Table 4 includes the various nucleating agents that have been used in the preparation of slag glass-ceramics.

TABLE 4

Nucleating Agents for Slag Glass-ceramics

COUNTRY	NUCLEATING AGENT
U.S.S.R. [2, 3, 6]	Oxides of Zinc, Iron, Manganese, Chromium
England [1]	Iron Oxides, iron ores, chrome ores, chrome oxide, titania, clacium fluoride, a combination of 6% titania and 0.5% chrome ore is the most effective.
Hungary [7]	Iron and Manganese Sulphides, ZrO_2, P_2O_5, NiO, V_2O_5, chromite, magnetite

An overview of nucleating agents, heat treatment, crystalline phases and physical properties of slag glass-ceramics is presented in Table 5.

Kislitsyn et al (2) have used Cr_2O_3 as the nucleating agent. They found that Cr_2O_3 concentration of 1.5 wt% is the most suitable. The glasses were melted at 1450 - 1470°C and the crystallization was completed at 900°C.

The composition and properties of the glass-ceramics by Kislitsyn et al (2) are given in Tables 6 and 7.

In the glass composition, the Cr_2O_3 together with iron oxides forms spinels in whose crystals the basic mineral phase (monoclinic pyroxenes of a complex composition) is formed.

Pyroxenic glass-ceramics have been studied by Kasyakin et al (10). Cr_2O_3, TiO_2 and a mixture of Cr_2O_3 and pyrites have been used as nucleating agents. It was found that .5 to 1.5 wt% of Cr_2O_3 gave fine grained glass-ceramics. Tables 8, 9 and 10 include the data on the heat treatment schedules, compositions and physicochemical properties of the glass-ceramics.

In another study (3), FeO and MnO have been used to replace the MgO and CaO in the crystalline lattice of pyroxene. The glass was prepared by melting at 1520 ±10°C for 5 hours, nucleated at 650°C for 1 hour and crystallized at 770°C for 1 hour. The product has the following properties:

Transverse bend strength (MPa) : 58
Microhardness (MPa) : 6573

TABLE 5

Slag Glass-ceramics (4,7,8,9,2)

Major Constituent and Concentration (wt.%)	SiO_2 (30-63), Al_2O_3 (5-30), CaO (9-47), MgO (up to 10, preferred at 5)
Nucleating Agents (Wt.%)	- Oxides of zinc, iron manganese, chromium, titanium. - Iron ores, chrome ores. - Calcium fluoride. - Heavy metal sulphides (0-15%)
Heat Treatment	- Melting : 1400 - 1600°C - Nucleation : 650 - 800°C - Crystallization: 800 - 1100°C
Crystalline Phase	Diopside, $CaMg(SiO_3)_2$ (9); Akermanite $Ca_2MgSi_2O_7$; Wollastonite, $CaSiO_3$; Anorthite, $CaAl_2Si_2O_8$; clinopyroxene, monoclinic pyroxene (2).
Physical Properties	- Density ~ 2.9 $g.cm^{-3}$ - Softening Temperature 770-1225°C - Vicker's hardness 750(9) - Moh's scale 8-8½ - Modulus of Rupture ~1400 $kg.cm^{-2}$ - Loss of Mass on Abrasion 0.179 $kg.cm^{-2}$ (2) - Acid resistance (96° H_2SO_4) 98.7

TABLE 6 (Ref.No.2)

Composition (Wt%) of Glass-Ceramics

Sl. No.	Oxides	Concentration Range
1	SiO_2	40.4 - 60.3
2	CaO	11.5 - 19.4
3	MgO	6.6 - 11.5
4	MnO	3.2 - 5.3
5	FeO	4.2 - 7.5
6	Al_2O_3	8.3 - 9.5
7	Na_2O	5.1 - 5.2

TABLE 7

Properties of Glass-Ceramics Developed by Kislitsyn et al (2)

Sl No.	Properties	Code Name of Glass-Ceramics	
		BM-40	Industrial Composition
1	Ultimate bend strength, MPa	80	90
2	Loss of mass on abrasion, Kg/m^2	0.179	0.201
3	Thermal-shock resistance, ^oC	400	150
4	Acid-resistance to 96% H_2SO_4	98.7	99.91
5	Alkali resistance to 35% NaOH	82	81.54
6	Density, g/cm^3	2.9	2.78

TABLE 8 (Ref.No. 10)

Waste Materials

Material	Wt. content, %							Calcination loss
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$K_2O + Na_2O$	SO_3	
Ash:								
Belovo SREPP	61.91	22.10	5.41	4.92	2.43	2.4	0.80	1.38
Novokemerovo HEPP	52.72	21.06	8.22	3.40	1.60	2.20	0.80	5.45
Tom'-Usinsk SREPP	61.15	25.94	6.93	3.14	1.12	1.18	0.54	8.12
Zapadno-Sibirskoe HEPP	56.51	21.03	8.91	5.06	3.04	2.63	2.41	1.58
Zapadno-Sibirskoe HEPP slag	58.16	18.41	6.73	2.41	4.58	2.0	0.95	—

TABLE 9 (Ref. No. 10)

Glass-Ceramics & Their Properties

Grade of ceramic glass	Wt. content, %									Physicochemical properties					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	SO_3	Cr_2O_3	TiO_2	density, g/cm^3	heat resistance, °C	hardness index, g/cm^2	corrosion resistance in relation to		
													96% H_2SO_4	1 N HCl	1 N NaOH
BII-2	49.67	15.53	6.59	18.17	3.51	1.91	0.58	1.80	—	2.78	420	0.0105	99.21	85.99	99.23
KV-1	47.38	9.32	6.23	18.70	2.43	1.58	0.64	0.57	13.87	3.02	420	0.0055	99.53	94.97	99.27
KV-2	43.53	14.64	7.20	21.34	2.60	3.22	1.90	0.64	—	2.82	480	0.0078	99.91	98.57	94.38	
№ 22222	45.00	16.08	6.91	23.09	4.29	1.29	0.74	0.56	—	3.07	470	—	99.24	70.54	99.22	
№ 6013	44.72	17.24	5.61	23.16	4.22	1.22	0.68	0.87	—	2.92	450	0.0058	99.82	92.27	99.08	
Commercial slag-based ceramic glass made by the Avrosteklo plant	49—63	5.4—10.7	0.1—10	22.9—29.6	1.3—12	2.6—5	—	0.1—2	—	2.6—2.9	200—350	0.015—0.025	99.8	98.0—99.8	74.7—98.0	

TABLE 10 (Ref. No. 10)

Heat Treatment Schedule

Grade of glass	Mode of heat treatment					
	I stage		II stages		III stages	
	t, °C	τ, h	t, °C	τ, h	t, °C	τ, h
BII-2	700	2	950	1	—	—
KV-1	720	1	980	1	—	—
KV-2	710	1	990	1	—	—
№ 6013	900	1	—	—	—	—
№ 22222	700	1	500	—	900	1

In the preparation of slag-ceramics, magnetite (Fe_3O_4) has also been used as a nucleating agent for pyroxene growth. The F^{3+}/Fe^{2+} ratio in the melt is crucial for the formation of magnetite.

Beall et al (11) have found that the best combination of properties of glass-ceramics was developed through heating well oxidised glasses (Fe_2O_3 : FeO >1) for 4 hours at 650°C and crystallizing the glass at 800°C for one hour. Figure 4 shows the ultrafine grained highly oxidised basalt glass-ceramics with clinopyroxene crystals.

5. PHYSICAL PROPERTIES AND MICROSTRUCTURE

One of the notable characteristics of glass-ceramics is their extremely fine grain size. Besides, the crystals are fairly uniform in size and they are randomly oriented.

Since the crystals in a glass-ceramics are formed by precipitation from a homogeneous liquid (glass) phase under conditions where there are usually no stresses that can cause alignment, they are randomly oriented. The absence of orientation means that the properties of a glass-ceramic are isotropic. Even though some of the crystals present may have different properties in different crystallographic directions these are averaged out in the glass-ceramic.

While the dense, fine texture of glass-ceramics serves to distinguish them from conventional ceramics and forms the basis which determines many of the special characteristics, the nature and proportions of the crystal phases present are extremely important in deciding the individual characteristics of a glass-ceramic.

Since the volume change which occurs during conversion from the glass state to the glass-ceramic is usually small, the density of the glass-ceramic will be close to the density of its parent glass. However, the difference of 2.8% in the density of glass and the glass-ceramic has been reported.

In one study (12) transmission electron microscopy, x-ray diffraction and infra-red spectroscopy have been employed to study the microstructure and crystallization of Li_2O-MgO-Al_2O_3-SiO_2 glass ceramics doped with < 2 wt% Fe_2O_3 with the addition of TiO_2, ZrO_2 and P_2O_5 as nucleating agents. Heat treatment of the glass at 830^oC for long times (> 100 h) leads to an intergrown microstructure. In this system, the microstructural changes were correlated with a peak shift effect in the x-ray diffraction pattern, a band broadening effect in the infra-red spectra. However, the microstructural changes were directly observed by transmission electron microscopy.

The elastic and the thermal properties of the residual glass and crystalline phases affect the strength of a glass-ceramic. In the MgO - SiO_2 - Al_2O_3 system, nucleated by TiO_2, the effects of the different crystalline phases, cordierite, cristobalite, magnesium aluminum titanate and rutile on the fracture strength of glass-ceramic has been described (13).

Shetty et al (14) have recently measured the strength of glass-ceramics using both 3 and 4 point bending tests. Grain-size dependence of fracture energy in ceramics has been described by Rice et al (15, 16). The stability of the glass phase in a glass-ceramic has been discussed by Raj.(17)

The effects of variation of the heat treatment cycle in modifying the microstructure and mineralogical constitution of glass-ceramics are well known. During heat treatment the chemical composition of the glass-ceramics remains unchanged, yet large variations in the crystallographic constitution

can occur. These changes are responsible for the change in the physical properties, such as mechanical strength.

Atkinson and McMillan (18) studied the effect of heat treatment on a glass composition (mole%) SiO_2 61.0, Li_2O 30.5, K_2O 1.5, Al_2O_3 1.0, P_2O_5 1.0, B_2O_3 5.0. The results are shown in Figure 5 and 6.

Abrasion resistance like hardness is not a fundamental physical characteristic of a material but rather it is a complex function of a number of physical properties which are combined in different degrees depending on the method of test.

The hardness measured on Moh's scale for the crystals generally found in glass-ceramics are given in Table 11.

The degree of abrasion-resistance of a material depends upon the grain size, hardness, shape, weight and the operating conditions, such as the atmosphere, the prevailing temperature, etc. McMillan (4) suggested that the abrasion resistance of a material under closely specified conditions may be taken as one measure of its hardness. Using Moh's scale glass-ceramics may reach hardnesses approximating those of corundum (Al_2O_3) and silicon carbide which are in the 9-9.5 range. Glass-ceramics may reach hardnesses considerably greater than those of glasses which are usually between 5 and 7.

In one study Nagwa et al (20) have studied the microhardness of glasses as a function of glass composition. It is mentioned that the microhardness of glass is linearly related to oxide compositions within a given phase field (21). Alteration in the glass compositions is expected to lead to

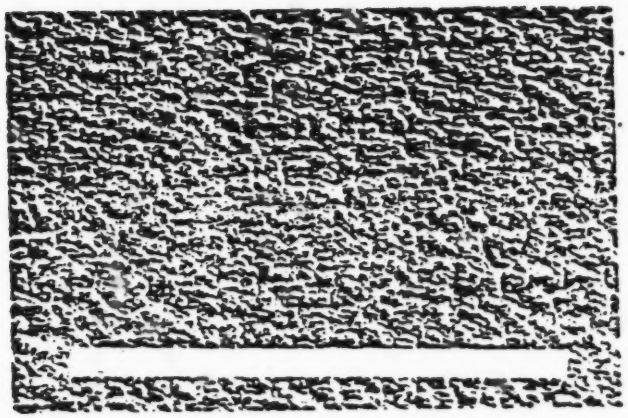

Figure 4: Ultra-fine-grained highly oxidized basalt glass ceramic with clinopyroxene crystals < 1000 A in size. Replica electron micrograph; bar = 1u m (Reference No. 11)

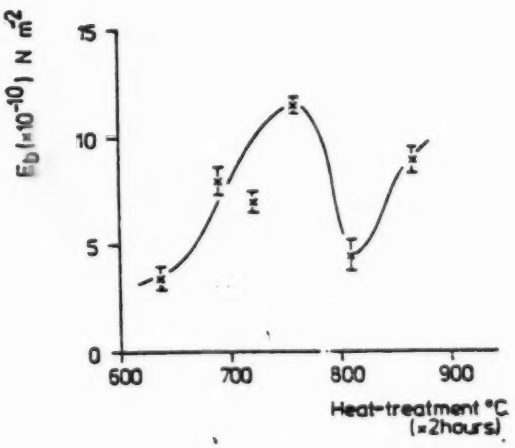

Figure 5: The variation of the Young's modulus, E_b, of the glass-ceramic with various 2h heat-treatment temperatures. (Reference No. 18)

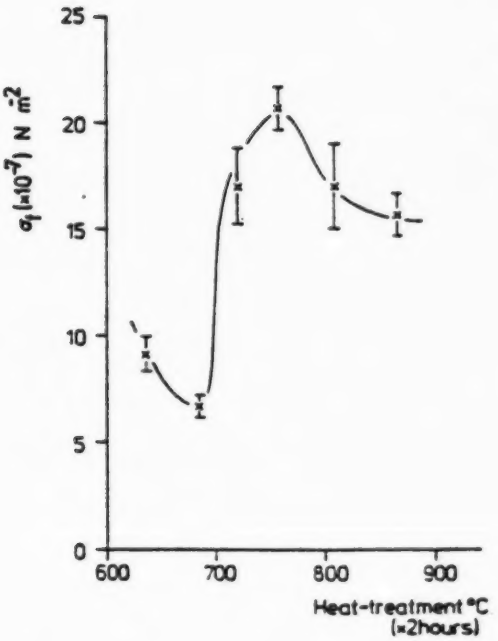

Figure 6: The variation of the modulus of rupture, σ_f, of the glass-ceramic with various 2h heat-treatment temperatures. (Reference No. 18).

TABLE 11 (Ref.No. 19)

*Hardness of Some Crystals

Crystal Phase	Hardness (Moh)
Beta-eucryptite ($Li_2O.Al_2O_3.SiO_2$)	6.5
Cordierite ($2MgO.2Al_2O_3.\ 5SiO_2$)	7 - 7.5
β-spodumene ($Li_2O.Al_2O_3.\ 4SiO_2$)	6.5 - 7.5
Celsian ($BaO.Al_2O_3.\ 2SiO_2$)	6 - 6.5
Anorthite ($CaO.\ Al_2O_3.\ 2SiO_2$)	6 - 6.5
Clinoenstatite ($MgO.SiO_2$)	5 - 6
Forsterite ($2MgO.\ SiO_2$)	7
Wollastonite ($Li_2O.\ 2SiO_2$)	4.5 - 5
Quartz SiO_2	7
Cristobalite SiO_2	6.5
Augite (Ca, Na) (Mg, Fe, Al) $(Si, Al)_2\ O_6$	5.5 - 6
Diopsite Mg Ca $Si_2\ O_6$	5.5 - 6.5
Fassaite $Ca(Mg, Fe^{3+}, Al)\ (Si, Al)_2\ O_6$	6

*Phases containing Al_2O_3 show better hardness which is directly proportional to abrasion resistance.

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a different phase substructure that would give the desired hardness value.

Apart from the crystalline phases, the nature of bonding between the phases, the residual glass, stresses, etc., will contribute to the mechanical and other properties of the glass-ceramics. More work is required to understand the relationship between hardness, abrasion resistance and microstructure of a glass-ceramic.

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